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A High-Level Computational Study on the Thermochemistry and Thermal Decomposition of Sulfur Mustard (2,2′-Dichloroethyl Sulfide): A Chemical Warfare Agent

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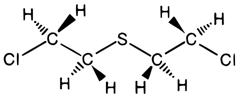
The calculations of enthalpies and free energies for various monomolecular decompositions of sulfur mustard using G2(MP2) theory have shown that noncatalytic thermal destruction of this chemical warfare agent apparently is not feasible at temperatures up to 1800 K at least. Environmentally robust decomposition/destruction demands operating conditions in excess of 2000 K to insure intrinsic safety in the absence of a catalyst. The preferable decomposition pathways involve C−C and C−S bond cleavages. The G2(MP2)-calculated enthalpy of formation of sulfur mustard is −36.86 kcal/mol for the lowest energy C_2 conformation.

1. Introduction

There are few organic compounds that have garnered the notoriety afforded "sulfur mustard" (2,2′-dichloroethyl sulfide). Sulfur mustard, **1**,



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is a vesicant or blistering chemical warfare agent, for which there still is no effective therapy.[1] It is one of the oldest chemical warfare agents that has been produced by man and was first introduced in 1917.[1d] Although this dehabilitating nerve agent is a liquid of low volatility, it is often referred to as "mustard gas". Sulfur mustard (HD) is a major component in stockpiles of chemical warfare agents that have been manufactured subsequently.[2] International meetings have been convened recently to discuss methods of destruction for HD and related agents.[2a] While incineration was chosen initially as the preferred method of disposal, alternative methods[2a,b] are now under consideration as local citizens groups have questioned the environmental integrity of incineration methods. Significant nonuniformities in the high temperature primary combustion region, as well as the exit zone, can arise even during quasi-steady processing.[3a] Temperature gradients[3b] can also have a deleterious effect upon the destruction removal efficiency (DRE) and produce products of incomplete combustion (PIC) that can rival or exceed the toxicity of the initial feed stream. Such monofunctional analogues of sulfur mustard as 2-chloroethyl ethyl sulfide that can be formed upon the thermal decomposition of sulfur mustard and 4-carboxybutyl 2-chloroethyl sulfide are also vesicants.[4]

Combustion is a process where compounds are broken down by high temperature oxidation and/or pyrolysis.[3d] Typical combustion reactions involve a spectrum of unimolecular, bimolecular, and higher order reactions with oxygen, oxygen-containing species, and substrate radical fragments.[3d] This raises an intriguing question as to the fate of toxic materials that can pass through the incinerator without experiencing the perturbative influence of such highly reactive species. At higher temperatures the thermal decomposition of mustard provides the chain initiation step resulting in the formation of radicals.[3d] These radicals can be involved in recombination reactions or be oxidized in the secondary thermal zone. What is the final disposition of HD that is simply exposed to the high temperature of the reaction zone? In this report we examine which chemical bonds would break initially in a pyrolytic mode and predict the anticipated fate of the initially formed radical fragments.

Another of the primary difficulties encountered in the destruction of "mustard" after decades of storage is that it rarely exists in a uniform physical state. "Mustard" that has been held in metal containers has become partly or even mostly gelled or crusty.[2a] Therefore, the application of traditional bimolecular chemical methods to destroy mustard (e.g., reaction with a strong aqueous base)[2b] is hampered by the absence of reliable, reproducible data on the chemistry of gelled or crusty "mustard". If specific chemical reactions that take place in the condensed phase are chosen to destroy "mustard", the intractability of the residual material often constitutes a major problem since the attacking reagent in bimolecular processes can not gain access to the reaction site.

Many studies on HD were made before highly sensitive modern analytical techniques became available in chemistry. Some of that research was performed without special care in the definition of experimental conditions and with a less than rigorous evaluation of the data. As a consequence, there are some gaps in the reliability of the chemistry of sulfur mustard.[2a] The data on the gas-phase enthalpies of formation and combustion of HD are not yet available[5] despite their importance for the evaluation of its destruction by a free radical oxidative process. The incompleteness of the thermochemical data sets for radical intermediates formed in the course of the thermal

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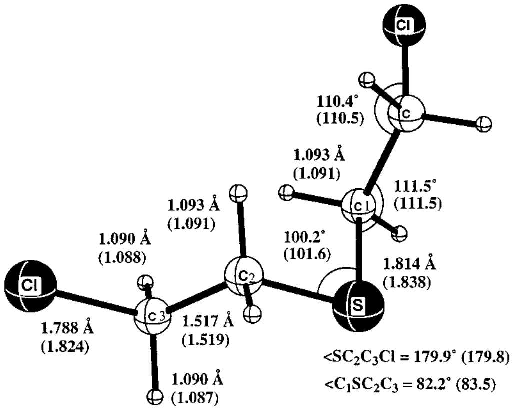

1b C_2

Figure 1. The lowest energy C_2 conformation (**1b**) of sulfur mustard optimized at the MP2(full)/6-31G(d) and B3LYP/6-311G(d,p) (values in parentheses) levels of theory.

decomposition of mustard results from the experimental difficulties in studying such short-lived intermediates. Theoretical methods have now reached a degree of reliability where they can provide an alternative source of data on the thermochemistry of chemical warfare agents.

There have been few computational studies of sulfur mustard[6−10] reported to date. In a pioneering study, Bartlett et al. calculated harmonic frequencies of **1a** at the HF/3-21G level.[6] The C−C, C−S, and C−Cl bond energies of sulfur mustard were computed by Politzer and Habibollahzadeh at the MP2/6-31G(d) level.[7] The episulfonium cation **2** formed from neighboring sulfur participation involving heterolytic C−Cl bond cleavage has been studied by Broch et al. using HF/6-31G(d) calculations.[8a] However, all of the above calculations were all carried out for the C_{2v} geometry (**1a**) of sulfur mustard. Recent calculations by Donovan and Famini[10a] have shown that while **1a** is the lowest energy conformer if molecular mechanics methods (MM2 and MM3) are used, AM1, HF/6-311G(d,p), MP2/6-31G(d), and MP2/6-311G(d,p)//HF/6-311G(d,p) calculations favor a C_2 structure (**1b**). The all-anti structure **1a** is 2.46 kcal/mol higher in energy than **1b** (Figure 1) at the MP2/6-311G(d,p)//HF/6-311G(d,p) level. Two other conformations are less than one kcal/mol higher in energy than C_2 structure (**1b**).[10a]

To evaluate the feasibility of the thermal destruction of sulfur mustard, reliable data on the thermochemistry of sulfur mustard and, particularly, on its bond dissociation energies, are required. Since the experimental data necessary to examine the thermochemistry of sulfur mustard are not available at the present time, we have carried out calculations using density functional theory (DFT)[11] and G2(MP2) theory.[12] DFT methods have gained great popularity in recent years because of their success in calculations of atomization energies,[13] heats of formation,[14] bonding energies,[15] proton affinities,[16] and harmonic frequencies of polyatomic molecules.[17] Among various proposed functionals, the Becke's three-parameter hybrid functional[18a,19a] combined with the Lee, Yang, and Parr (LYP) correlation functional[18b] and denoted as B3LYP,[19b] appears to be the best to date. We have studied the thermochemistry of the decomposition of **1b** using G2(MP2) theory.[12] Applications of G2(MP2) theory have a demonstrated performance in calculations of heats of formation, ionization energies, electron affinities, bond energies, proton affinities, and acidities.[20] The G2(MP2) theory tested on a total of 125 energies (dissociation energies, ionization energies, electron affinities, and proton affinities) having well-established experimental values, gives an average absolute deviation from experimental atomization energies of 1.21 kcal/mol.[12,20] As we show in the present study, only high-level calculations are capable of providing accurate data on the thermochemistry of sulfur mustard, particularly on its bond dissociation energies.

The high toxicity of sulfur mustard is ascribed to the formation of the cyclic episulfonium cation **2** through anchimeric assistance of the β-sulfur atom displacing a chloride ion in a solvolytic process.[21] This highly reactive episulfonium cation which was computationally studied earlier at the HF level,[8b,c] is an exceptional bifunctional alkylating agent and its principal target when it enters cells is DNA. Therefore, we have also addressed the question whether episulfonium cation **2** is the lowest isomer of $ClC_4H_8S^+$ or if an open-chain cation can compete with **2** in stability.

2. Computational Methods

Ab initio molecular orbital calculations[22] were performed with the GAUSSIAN 94 system of programs.[23] The Becke's three-parameter hybrid functional combined with the Lee, Yang, and Parr (LYP) correlation functional,[18b] denoted B3LYP,[19b] was employed in the calculations using density functional theory (DFT). Geometries were optimized[24] using the 6-311G(d,p) basis[22] set in B3LYP calculations and the 6-31G(d) basis set[22] in calculations at the MP2 level. The MP2/6-31G(d)-calculated geometries were used for computing G2(MP2) energies. G2(MP2) theory[12] corresponds effectively to the QCISD(T)/6-311+G(3df,2p)//MP2/6-31G(d) level with incorporation of HF/6-31G(d) scaled zero-point energies and so-called higher level corrections. A scaling factor of 0.9614 was used for the B3LYP/6-311G(d,p) harmonic frequencies.[25] Enthalpy temperature corrections were derived using harmonic frequencies which were computed at the HF/6-31G(d) level and scaled by 0.8929 according to the G2(MP2) method.[12] Standard statistical thermodynamics formulas, using the rigid-rotor and harmonic-oscillator approximations, were employed in the calculations.[22] Corrections for internal rotation are discussed in the text. Theoretical enthalpies of formation at 0 K and 298 K, ΔH_{f_0} and $\Delta H_{f_{298}}$, respectively, were derived from calculated G2(MP2) atomization energies (see ref 26 for details) for the species at 0 or 298 K and standard experimental enthalpies of formation for the atoms at 0 or 298 K, respectively. The compendium of Lias et al.[27a] was used as the source of thermodynamical data unless stated otherwise. Experimental temperature corrections for atoms, taken from ref 27b, were used. Throughout the text, bond lengths are in angstroms and bond angles are in degrees. The enthalpies and free energies for atoms at 1800 K taken from ref 27b were used in calculations of the enthalpies and free energies at 1800 K for the decomposition reactions of sulfur mustard and those species that are formed as products.

3. Results and Discussion

Geometry of Sulfur Mustard. We have found that the C_2 structure **1b** of sulfur mustard is 2.24 and 1.85 kcal/mol lower in energy than the C_s structure **1a** at the B3LYP/6311G(d,p) and B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p) levels, respectively. Therefore, we have considered only structure **1b** in further discussions. Its geometry optimized at the B3LYP/6-311G(d,p) level is close to the MP2/6-31G(d) calculated geometry even though different basis sets are employed (Figure 1). The C−C bond lengths in structure **1b** (1.519 Å at the B3LYP/6-311G(d,p) level) are shortened as compared with that

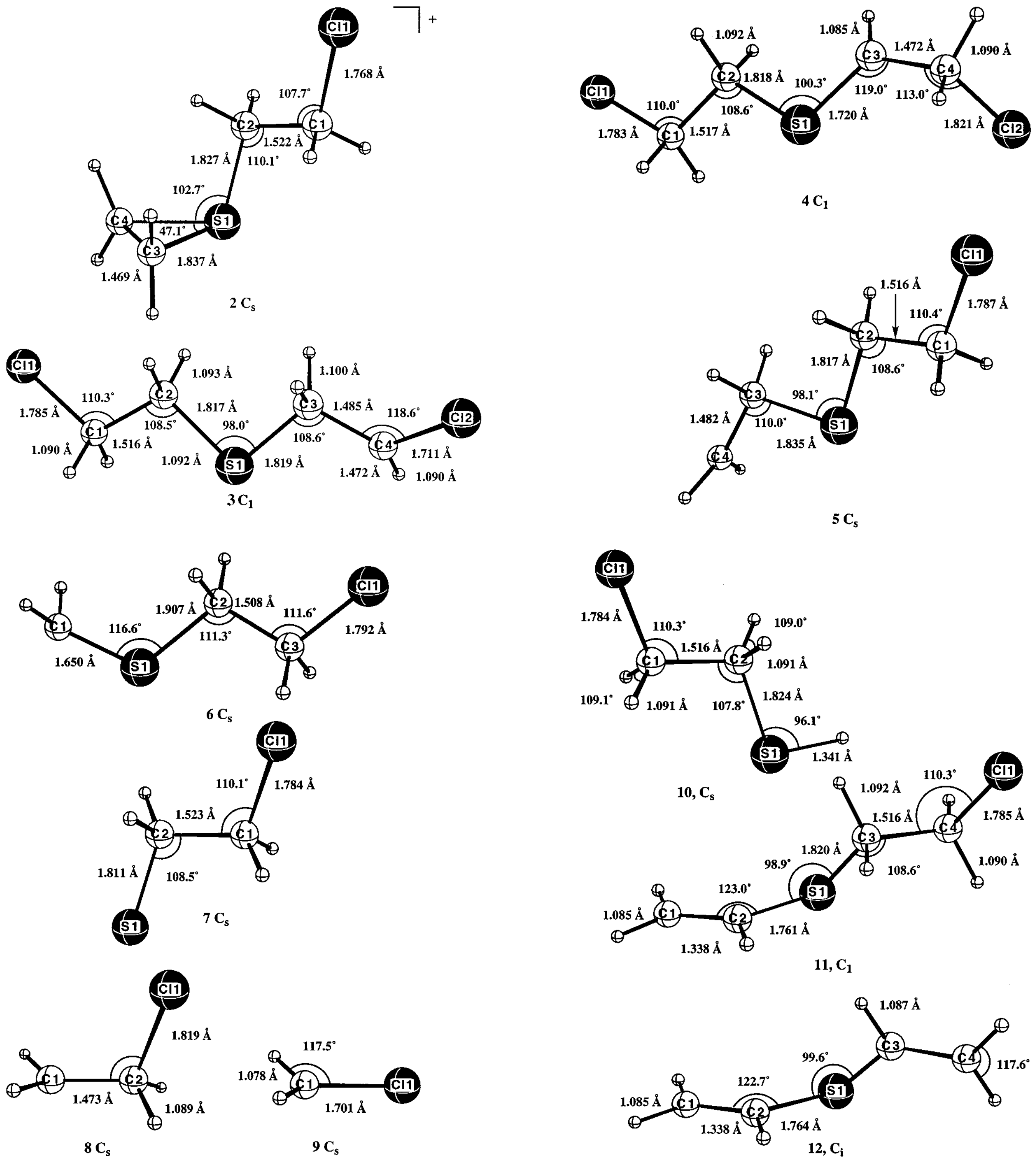

Figure 2. Selected geometrical parameters of the products of C−Cl, C−S, C−C, and C−H bond cleavages in sulfur mustard (**1b**) optimized at the MP2(full)/6-31G(d) level of theory.

in ethane (the experimental gas phase electron diffraction (ED) value[28] is 1.5326 Å) and in ethanethiol (1.529 Å).[29] In contrast, the B3LYP calculated C−Cl bond lengths (1.824 Å) are slightly elongated when compared with those in methyl and ethyl chloride (their experimental values are 1.776[30] and 1.789 Å,[29] the MP2(full)/6-31G(d)-optimized value is 1.788 Å). This small difference may reflect a long-range interaction with the β-sulfur atom. The C−S bond length and the CSC valence angle in **1b** are close to those in dimethyl sulfide (1.802 Å and 98.87°, respectively).[29] Our attempts at the geometry optimization of open-chain isomers[8] of cyclic cation **2** at the MP2/6-31G(d) and B3LYP/6-31G(d) levels eventually led to **2**. The geometries of **2** and other products of sulfur mustard decomposition are shown in Figure 2.

The natural population analysis (NPA)[31] of the wave function calculated at the B3LYP/6311+G(3df,2p) level for **1b** shows that the carbon atoms bear negative charges. The sulfur has a positive charge of 0.2137 and this should make it easier for the sulfur mustard molecule to form the sulfonium cation intermediate **2** in the hydrolysis reaction.

TABLE 1: Harmonic Frequencies (in cm^{-1}) of the C_2 and C_{2v} Structures of Sulfur Mustard Calculated at the B3LYP/6-311G(d,p) Level and the Experimental Values[a]

calculated frequency (unscaled, C_2)	calculated frequency (scaled, C_2)[b]	calculated frequency (unscaled, C_{2v})	calculated frequency (scaled, C_{2v})	experimental frequency
3164 (a)	3041 (5)	3157 (a_2)	3035	
3163 (b)	3040 (5)	3156 (b_1)	3034	3003
3120 (a)	2999 (1)	3110 (a_2)	2990	
3119 (b)	2999 (1)	3107 (b_1)	2987	2964
3100 (b)	2980 (23)	3095 (b_2)	2976	2933
3099 (a)	2979 (3)	3095 (a_1)	2976	2915
3072 (a)	2953 (1)	3058 (b_2)	2940	
3071 (b)	2952 (7)	3056 (a_1)	2938	2867
1487 (b)	1429 (12)	1497 (a_1)	1439	1443
1486 (a)	1429 (0)	1494 (a_1)	1436	1423
1475 (a)	1418 (0)	1494 (b_2	1436	1406
1467 (b)	1410 (6)	1489 (b_2)	1431	1384
1331 (a)	1280 (11)	1348 (a_1)	1296	1295
1331 (b)	1280 (16)	1332 (b_2)	1281	1278
1311 (a)	1260 (1)	1302 (b_1)	1252	1268
1301 (b)	1251 (0)	1299 (a_2)	1249	
1265 (a)	1216 (7)	1269 (a_1)	1220	1216
1241 (b)	1193 (37)	1237 (b_2)	1189	1208
1161 (a)	1115 (11)	1146 (b_1)	1102	1142
1143 (b)	1099 (1)	1140 (a_2)	1096	1134
1047 (a)	1006 (1)	1068 (a_1)	1027	1037
1043 (b)	1003 (4)	1036 (b_2)	996	1021
1010 (a)	971 (0)	1000 (b_1)	961	972
955 (b)	917 (0)	975 (a_2)	937	937
769 (a)	738 (5)	793 (b_1)	762	758
749 (b)	720 (1)	783 (a_1)	753	734
733 (b)	705 (5)	780 (a_2)	750	
724 (a)	695 (10)	752 (b_2)	723	
688 (b)	661 (118)	705 (b_2)	678	702
675 (a)	649 (47)	691 (a_1)	664	690
331 (a)	318 (0)	330 (b_2)	317	344
312 (b)	300 (1)	322 (a_1)	310	304
229 (a)	220 (2)	213 (a_1)	205	245
224 (b)	214 (17)	206 (b_2)	198	240
192 (a)	185 (0)	105 (b_1)	101	
108 (b)	104 (3)	104 (a_2)	100	
87 (b)	84 (0)	60 (a_1)	58	
79 (a)	76 (2)	35 (a_2)	34	
33 (a)	32 (1)	31 (b_2)	30	

[a] Calculated frequencies are scaled with 0.9614 see the text. The experimental frequencies were matched according their values as done in ref 10. [b] IR intensities are given in parentheses (in KM/mol).

Harmonic Frequencies of the Most Stable Conformer of Sulfur Mustard. There is at least a dozen conformers of mustard with energies that lie within a range of 4 kcal/mol.[10] The energy differences between some of them are less 1 kcal/mol at the MP2/6-31G(d) level.[10] The experimental IR and Raman spectra of mustard suggest the existence of an equilibrium mixture of conformations.[32] The harmonic vibrational frequencies calculated for the C_2 and C_{2v} conformations of mustard at the B3LYP/6-311G(d,p) level (Table 1) are in good agreement with the experimental values (taking into account that they correspond to a complex mixture of conformations).[32] The vibrational frequencies calculated earlier at the HF/6-311G(d,p) level[10a] also agree well with the experimental data. This allows the expectation that the HF/6-31G(d) vibrational frequencies used in calculations of the mustard thermochemistry at the G2(MP2) level are reliable.

For further assessment of the accuracy of the B3LYP/6-311G(d,p) and HF/6-31G(d) vibrational frequencies, following Sosa, Bartlett et al.,[6] we have compared the calculated frequencies for *gauche*-ethanethiol with the experimental data (Table 1S, Supporting Information). The calculated frequencies demonstrate very good agreement with the experimental values.

TABLE 2: Calculated G2 and G2(MP2) Gas-Phase Enthalpies of Formation (in kcal/mol) of 1,2-Dichloroethane and Related Prototypical Molecules as Well as the Experimental $\Delta H_{f_{298}}$ Values

molecule, method	ΔH_{f_0}	$\Delta H_{f_{298}}$
methyl chloride, G2	−18.56	−20.54
methyl chloride, G2(MP2)	−19.17	−21.14
methyl chloride, exptl	−17.7[a]	−19.6 ± 0.2[a]
ethyl chloride, G2	−24.06	−27.64
ethyl chloride, G2(MP2)	−24.46	−28.03
ethyl chloride, exptl		−26.83 ± 0.18[b]
methanethiol, G2	−2.86	−5.25
methanethiol, G2(MP2)	−3.57	−5.97
methanethiol, exptl	−2.9[c]	5.5 ± 0.1[c]
ethanethiol (gauche),[d] G2	−7.34	−11.31
ethanethiol (gauche), G2(MP2)	−7.85	−11.82
ethanethiol, exptl		−11.03[e]
1,2-dichloroethane, G2	−30.24	−33.45
1,2-dichloroethane, G2(MP2)	−31.71	−34.92
1,2-dichloroethane, exptl		−29.98 ± 0.25[f] −30.8[g]
1,2-ethanediol,[h] G2	−90.1	−94.92
1,2-ethanediol, G2(MP2)	−91.08	−95.90
1,2-ethanediol, exptl		−94.26 ± 0.67[i]

[a] Taken from ref 34. [b] Taken from ref 35. [c] Taken from ref 27a. [d] C_s structure is 0.5 kcal/mol higher in energy at G2 level. [e] Ref 36, this value is recommended by the NIST Thermochemical Database.[37] [f] The original value (−30.18 ± 0.25 kcal/mol at 548 K) given in ref 38a was reanalyzed by Cox and Pilcher (ref 38b). [g] Taken from ref 39. The two experimental $\Delta H_{f_{298}}$ values are recommended by the NIST Thermochemical Database.[37] [h] tGg′ conformer, see ref 40. [i] Taken from ref 41.

Enthalpies of Formation and Bond Enthalpies of Mustard and Its Decomposition Products. *(a) Assessment of the Performance of G2(MP2) Theory in Calculations of Enthalpies of Formation and Bond energies of Chloro- and Sulfur-Containing Species.* In most cases using G2(MP2) theory leads to computed thermochemical values that are close to those calculated at the G2 level.[12] Applications of G2 theory in the thermochemistry of chlorine[33a−c] and sulfur[33d]-containing compounds demonstrate its capability of providing highly accurate results. We have calculated enthalpies of formation and bond dissociation energies (BDE) for some prototypical molecules, which are similar to sulfur mustard and its products of dissociation, for which experimental data are available (Tables 2 and 3). The G2 and G2(MP2) calculated energies of these molecules are given in Table 2S (Supporting Information). The G2 and G2(MP2) data are very close to each other and to the experimental values with the exception of 1,2-dicholoroethane. The experimental estimate of its enthalpy of formation ($\Delta H_{f_{298}}$) differs by 3−4 kcal/mol from the G2 and G2(MP2) calculated values that are also in agreement (Table 2). We have calculated the enthalpy of formation for 1,2-ethanediol for which more recent experimental data are available.[41] The calculated and experimental $\Delta H_{f_{298}}$ values are in very good agreement (Table 2). Therefore, we suggest that the earlier experimental $\Delta H_{f_{298}}$ value for 1,2-dichloroethane be reexamined. All this assures that the G2(MP2) data on the thermochemistry of mustard, $Cl(CH_2)_2S(CH_2)_2Cl$, should possess a similar high level of accuracy. We have also calculated the enthalpy of formation for the highly toxic "half-mustard" ($HSCH_2CH_2C1$, **10**). The ΔH_{f_0} and $\Delta H_{f_{298}}$ values are −14.65 and −18.14 kcal/mol, respectively, using G2(MP2) theory.

Comparison of the G2 and G2(MP2) calculated C−Cl, C−S, C−C, and C−H bond energies in prototypical sulfur- and chlorine-containing species with the experimental values demonstrates the performance of the G2(MP2) theory (Table 3). The maximal absolute difference between the G2 and G2(MP2)

TABLE 3: Calculated G2 and G2(MP2), as Well as Experimental Bond Dissociation Enthalpies (D_0, in kcal/mol) for C−Cl, C−C, C−S, and C−H Bond Cleavages in Prototypical Molecules[a]

molecule, method\bond	C−Cl	C−C	C−S	C−H
sulfur mustard, G2(MP2)	87.95	85.06	78.48	94.04[b]
C_2H_5Cl, G2	85.06	89.51		102.93[c]
C_2H_5Cl, G2(MP2)	86.30	89.16		102.08
C_2H_5Cl, exptl	82.9 (0 K)	89.6 (298 K)		
CH_3Cl, G2	82.89			99.90
CH_3Cl, G2(MP2)	83.97			99.29
CH_3Cl, exptl	82.3 (0 K)			99.7 (298 K)
C_2H_6, G2		88.30		100.86
C_2H_6, G2(MP2)		88.55		101.00
C_2H_6, exptl		87.60 (0 K)		100.1 (298 K)
CH_3SH, G2			73.04	
CH_3SH, G2(MP2)			73.96	
CH_3SH, exptl			73.6 (298 K)	
C_2H_5SH, G2		83.93	74.19	
C_2H_5SH, G2(MP2)		84.04	75.28	
C_2H_5SH, exptl			72.3 (298 K)	
H_3CSCH_3, G2			72.67	
$ClCH_2CH_2Cl$, G2	86.06	89.65		
$ClCH_2CH_2Cl$, G2(MP2)	86.29	88.68		
$HSCH_2CH_2Cl$, G2(MP2)		83.10	74.80	
$H_3CSCH_2CH_2Cl$, G2(MP2)			75.59[d]	94.55[e]

[a] Experimental D_0 values were derived using the data from ref 27. [b] For the α-CH bond cleavage in sulfur mustard. [c] For the H−CH_2CH_2Cl bond cleavage. The G2 calculated C−H bond energy for the H−CH(Cl)CH_3 bond cleavage is 98.98 kcal/mol. [d] For the H_3C−SCH_2CH_2Cl bond cleavage. [e] For the H−$CH_2SCH_2CH_2Cl$ bond cleavage.

TABLE 4: Bond Dissociation Energies, D_e, (in kcal/mol) for the Homolytic C−Cl, C−S, and C−C Bond Cleavages in the Sulfur Mustard Molecule Calculated at Various Computational Levels[a]

method\bond	C−Cl	C−C	C−S
Sulfur Mustard			
MP2/6-31G(d)[b]	84.1	92.8	74.4
MP2/6-311G(d,p)	87.97	95.85	80.69
MP2/6-311+G(3df,2p)	93.42	95.11	84.38
QCISD(T)/6-311G(d,p)	83.71	90.04	75.93
G2(MP2)[c]	92.05	92.19	82.52
Ethyl Chloride			
MP216-311G(d,p)	86.4	98.7	
MP2/6-311+G(3df,2p)	91.8	99.3	
QCISD(T)/6-311G(d,p)	82.6	94.6	
G2(MP2)[c]	90.9	98.0	
exptl, D_e[d]	87.5	98.5	

[a] D_e values were calculated at the MP2/6-31G(d) geometries. [b] MP2/6-31G(d) data were taken from ref 7. [c] G2(MP2) D_e values were calculated using G2(MP2) energies without the ZPE corrections. [d] Experimental D_e values were derived from the experimental D_0 values[27a] using the zero-point energies calculated at the HF/6-31G(d) level.

D_o values is 1.3, 1.0, and 0.9 kcal/mol for C−C, C−Cl, and C−H bonds, respectively. For the C−S bond in ethanethiol, the difference is 1.1 kcal/mol (Table 3). Could a lower level of theory be capable of giving accurate values for these bond energies? As seen from inspection of the C−C, C−Cl, C−S, and C−H bond energies in mustard, calculated at various levels of theory (Table 4), higher levels of theory are indeed required to obtain accurate BDE estimates. The calculated bond energies are also very sensitive to the quality of the basis set. The extension of the basis set from the 6-31G(d) to the 6-311+G(3df,2p) basis set at the MP2 level results in an increase in the D_e values of up to 10 kcal/mol. A comparison of the D_e values calculated at the MP2/6-311+G(3df,2p), QCISD(T)/6-311G(d,p), and G2(MP2) levels (Table 4) shows that, while the BDE for the C−C bond is treated reasonably well, for C−S and C−Cl cleavages in sulfur mustard the QCISD(T) level of theory may be not sufficient to provide reliable results if only a moderately sized basis set is used. A comparison of the C−Cl and C−C bond dissociation energies D_o in ethyl chloride calculated at various levels of theory with the experimental values (Table 4) confirms the need of using a high level of theory. Therefore, the calculations of bond cleavage resulting in open-shell fragments having an adjacent lone-pair of electrons becomes problematic in the absence of an extended basis set and electron correlation corrections. Another interesting point is that while the G2(MP2) D_e(C−Cl) and D_e(C−C) values for sulfur mustard are close to each other (Table 4), the D_o(C−C) value is smaller than the D_o(C−Cl) estimate (Table 5).

(b) Enthalpies of Formation and Bond Dissociation Energies of Sulfur Mustard and Products of Its Decomposition. The G2(MP2) calculated energies of sulfur mustard and the products of its dissociation are listed in Table 3S (Supporting Information). The G2(MP2) calculated enthalpies of formation of sulfur mustard ($\Delta H_{f_{298}} = -36.86$ kcal/mol) and radical fragments formed by C−C, C−H, C−S, and C−Cl bond cleavage are given in Table 6. The enthalpy of formation of sulfur mustard is negative. Therefore, its decomposition into its elemental species would not be accompanied by the release of heat. However, if other products of the decomposition of sulfur mustard have more negative enthalpies of formation, such reactions would be exotherrnic. The characteristic of a reacting compound that mainly determines the heat release is its chemical composition and not its enthalpy of formation.[3d] The G2(MP2) calculated C−C, C−Cl, C−S, and C−H bond energies in sulfur mustard are listed in Table 5.

There are no experimental data on the enthalpies of formation of the fragments and molecules which derive from the various bond cleavages in sulfur mustard (Table 5) except the $\Delta H_{f_{298}}$ value for the chloromethyl radical (31 kcal/mol).[27a] This estimate does not agree with other, more recent, experimental estimates of the $\Delta H_{f_{298}}$ (H_2CCl) that are 27 ± 2 kcal/mol[42a] and 28.0 ± 0.7 kcal/mol.[42b] The G2(MP2) value of the $\Delta H_{f_{298}}$ (H_2CCl) in the present study (27.05 kcal/mol, Table 6) is in excellent agreement with these more recent experimental estimates.

The G2(MP2) D_o values for mustard decrease in the order C−H > C−Cl > C−C > C−S, whereas for the set of the

TABLE 5: Calculated G2(MP2) Bond Dissociation Enthalpies, Gibbs Free Energies (in kcal/mol), and Entropy Changes for the C−Cl, C−S, and C−C Bond Cleavage in the Sulfur Mustard Molecule[a]

bond	D_o (0 K)	D_o (298 K)	ΔG (298 K)[a]	D_o (1800 K)	ΔG (1800 K)
C−Cl (homolytic cleavage)	88.0	89.3	77.8	90.1	19.3
C−Cl (heterolytic cleavage)	147.8	148.2	140.0	147.4	101.5
C−C(homolytic cleavage)	85.1	85.8	71.7	98.0	−0.7 (4.3)[b]
C−S (homolytic cleavage)	78.5	79.1	65.4	74.9	1.8 (6.8)[b]
C−H (homolytic cleavage)[c]	94.0	95.7	85.3	98.5	29.8
C−H (homolytic cleavage)[d]	100.7	102.4	92.1	105.2	37.2

[a] Without correction for internal rotation. [b] ΔG values with an estimated correction for internal rotation (see text) are given in parentheses. [c] Energy of the $ClCH_2CH(-H)SCH_2CH_2Cl$ bond. [d] Energy of the $ClCH(-H)CH_2SCH_2CH_2Cl$ bond.

TABLE 6: Calculated G2(MP2) Gas-Phase Enthalpies of Formation (in kcal/mol) of Sulfur Mustard (2,2′-Dichlorodiethyl Sulfide) (1b), the Products of C−Cl, C−S, and C−C Bond Cleavages in 1b, and of "Half-Mustard"

sulfur mustard and its fragments	ΔH_{f_0}	$\Delta H_{f_{298}}$
2,2′-Dichlorodiethyl Sulfide, **1b** C_2	−30.89	−36.86
$ClCH_2CH_2SCH_2CH_2^+$ Cyclic Cation, **2** C_s	171.83	165.94
$ClCH_2CH_2SCH_2CClH^\bullet$ Radical, **3** C_1	18.15	13.43
$ClCH_2CH_2SC(H^\bullet)CH_2$ Radical, **4** C_1	11.51	6.74
$ClCH_2CH_2SCH_2CH_2^\bullet$ Radical, **5** C_s ($^1A'$)	28.48	23.41
$ClCH_2CH_2SCH_2^\bullet$ Radical, **6** C_s ($^2A''$)	25.69	21.92
$ClCH_2CH_2S^\bullet$ Radical, **7** C_s ($^2A'$)	22.13	19.16
$ClCH_2CH_2^\bullet$ Radical, **8** C_s ($^2A'$)	25.45	23.05
$ClCH_2^\bullet$ Radical, **9** C_s ($^2A'$)	28.48	27.05
$HSCH_2CH_2Cl^\bullet$ **10** C_s	−14.65	−18.14

prototypical molecules, the bond energies D_o decrease in order C−H > C−C > C−Cl > C−S. The D_o (298 K) values for **1b** are in the same relative order, C−H > C−Cl > C−C > C−S, as the D_o(0 K) values (Table 5). The most interesting finding is that the C−C bond in sulfur mustard is weaker than the C−Cl bond. As seen from Tables 3 and 5, the C−Cl bond energies increase from methyl chloride to ethyl chloride to sulfur mustard with increasing carbon atoms. A similar trend is observed for the C−S bond energies as the chain length increases. In contrast, the C−C bond dissociation energy in sulfur mustard is smaller than the BDE(C−C) values in ethyl chloride and ethane. This is likely a reflection of the greater stabilization energy of the $ClCH_2CH_2SCH_2$ radical (**5**) with respect to methyl radical. This suggestion is confirmed by the stabilization energy (9.5 kcal/mol) calculated at the G2(MP2) level (eq 1). The stabilization of **5** is apparently caused by the

$$ClCH_2CH_2SCH_2\ (\mathbf{5}) + CH_4 \rightarrow CH_3SCH_2CH_2Cl\ (\mathbf{13}) + CH_3 \quad (1)$$

$$HSCH_2 + CH_4 \rightarrow CH_3SH + CH_3 \quad (2)$$

$$ClCH_2CH_2 + CH_4 \rightarrow CH_3CH_2Cl + CH_3 \quad (3)$$

$$ClCH_2 + CH_4 \rightarrow CH_3Cl + CH_3 \quad (4)$$

donor effect of the lone pairs of the α-sulfur. Indeed, the C−C bond energy (D_o) in ethanethiol (84.04 kcal/mol using the G2(MP2) theory) is close to the D_o(C−C) energy in sulfur mustard (85.06 kcal/mol) and is smaller than that in ethyl chloride (89.16 kcal/mol, Table 3). The stabilization energy of $HSCH_2$ (8.8 kcal/mol at the G2(MP2) level, eq 2) is close to that for **5**.

The G2(MP2) radical stabilization energies for CH_2CH_2Cl and CH_2Cl (eqs 3 and 4) are smaller (1.9 and 4.7 kcal/mol).

TABLE 7: Calculated G2 and G2(MP2) Enthalpy and Gibbs Free Energy for the C−Cl Bond Dissociation in Methyl Chloride as Well as the Experimental Values (in kcal/mol)

H_3C-Cl	G2(MP2)	G2	exptl[a]
ΔH (298 K)	85.74	84.65	83.8
ΔH (1800 K)	87.41	86.33	85.3
ΔG (298 K)	76.51	75.43	74.9
ΔG (1800 K)	25.14	24.05	25.7

[a] Experimental values were derived using the HSC 2.0 program.[44]

Gibbs Free Energies For the Initial Decomposition of Sulfur Mustard. A temperature of 500 °C is generally considered to be sufficient to effect bond isomerization and thermal cracking of hydrocarbons; such processes typically take place under conditions that promote second-order reactions. Metal catalysis can also greatly facilitate thermal rearrangement/degradation processes. Decomposition of organic waste in liquid metals has been recently developed as an industrial process.[43] We address the question here whether the thermal decomposition of sulfur mustard is feasible at high temperatures (1800−2200 K) in the absence of any catalysis. If the decomposition of mustard at these temperatures is not spontaneous (ΔG < 0), it could remain as an intact mustard in an incineration process.

Extrapolation of standard BDEs to high temperatures requires taking into account the effects of entropy and, therefore, the free energies of the bond dissociation processes become important. First of all, we discuss sources of possible uncertainties in the calculated free energies for the high temperature decomposition of sulfur mustard.

(a) Estimate of the Accuracy of Calculated Gibbs Free Energies for Mustard Decomposition at High Temperatures. The existence of low-lying electronic states of radicals formed as a result of high temperature bond cleavages in mustard is a source of uncertainty in the computed ΔS and, eventually, in ΔG values. Low-lying electronic energy levels of these radicals have to be known to calculate electronic contributions to their entropies. To estimate an error due to neglecting such contributions, we calculated the G2 enthalpy, entropy, and Gibbs free energy for the C−Cl bond cleavage in methyl chloride. The calculated values show very good agreement with the experimental data both at 298 K and 1800 K (Table 7). However, we should note that radicals formed in the thermal decomposition of mustard such as CH_2Cl, CH_2CH_2Cl, SCH_2CH_2Cl, and others differ from CH_3 and that the errors caused by neglecting electronic contributions to their entropies can be larger than those found for the dissociation of methyl chloride.

One more factor that can contribute to the uncertainty of the calculated ΔG values is treatment of internal rotation for high temperature processes. Using the harmonic oscillator approximation for treating internal rotation at high temperature can lead to significant errors.[45] To estimate the magnitude of such an error, we calculated the free energy for the C−C bond dissociation of ethane for which the experimental values are available. The correction for hindered rotation at 1000 K to

TABLE 8: Calculated G2 and G2(MP2) Enthalpy and Gibbs Free Energy for the C−C Bond Dissociation of Ethane as Well as the Experimental Values (in kcal/mol)

H_3C-CH_3	G2	exptl
ΔH (298 K)	90.8	89.9[a]
ΔH (1000 K)	92.2	91.1
ΔG (298 K)	78.8	78.5
ΔG (1000 K)	48.4 (48.7)[b]	50.1

[a] Experimental values were derived using the HSC 2.0 program.[44] [b] ΔG value corrected for the hindered internal rotation in ethane is given in parentheses. This correction was calculated using the tabulated free energy differences for hindered rotation and harmonic oscillator given in ref 46. At 1000 K, $RT = 1.99$ kcal/mol that is smaller than the experimental value for the internal rotation barrier (V) in ethane which is 2.882 ± 0.010 kcal/mol[47] (The G2 calculated barrier is 2.79 kcal/mol). The reduced moment of inertia in ethane is 2.491×10^{-47} kg m^2 (ref 48) and the free rotor partition function (Q_r) for the methyl group is 4.64 at 1000 K ($1/Q_r = 0.22$). At 1800 K, $RT = 3.6$ kcal/mol. Therefore, the free rotor model can be used for the internal rotation in ethane at this temperature. The correction to the ΔG value calculated using the partition functions for the free rotor and harmonic oscillator (the vibrational frequency corresponding to the internal rotation in ethane is 293 cm^{-1} at the HF/6-31G* level (scaled with 0.8929)) is 1.36 kcal/mol. Applying this correction to the G2 computational results on the dissociation of ethane leads to the $\Delta G(1800\ \text{K}) = 15.3$ kcal/mol.

TABLE 9: Calculated G2(MP2) Enthalpy and Gibbs Free Relative Energies of the *trans* and *gauche* Rotamers and the Transition Structures of 1,2-Dichloroethane (in kcal/mol)

$H_2ClC-CClH_2$	ΔE (G2(MP2), 0 K)	ΔH (G2(MP2), 298 K)	ΔG (G2(MP2), 298 K)
trans (180°)	0	0	0
gauche (68.1°)	1.2	1.1[a,b]	0.8[b]
eclipsed C_{2v} (0°)	8.6	8.1[b]	8.6[b]
eclipsed (119.4°)	4.6	4.1[b]	4.7

[a] Experimental energy difference between the *gauche* and *trans* rotamers is 1.05 ± 0.10 kcal/mol,[49b] in excellent agreement with the G2(MP2) results. [b] Values are given without corrections for internal rotation.

the ΔG value of the C−C bond cleavage in ethane is 0.3 kcal/mol and the G2 calculated ΔG value (48.7 kcal/mol) is close to the experimental value (50.1 kcal/mol; Table 8).

We have chosen 1,2-dichloroethane as a prototypical molecule with two chlorines to model the effect of C−C internal rotation in sulfur mustard on the free energies of its thermal decomposition. Calculations on the thermochemistry of the dissociation of 1,2-dichloroethane into two molecules of chloromethyl radical should address the internal rotation in $C_2H_4C1_2$. Experimental data show that the *trans* rotamer of 1,2-dichloroethane is more stable than the *gauche* one in the gas phase, although this relative energy order is inverted in the condensed phase.[49] The G2(MP2) calculated energy difference between the *gauche* and *trans* rotamers agrees well with the experimental value (Table 9). Even at 1800 K the internal rotation in 1,2-dichloroethane is not yet free ($RT = 3.6$ kcal/mol, whereas the rotational barrier height V_o is 4.6 kcal/mol). There are several formulas suggested for the correction to the thermodynarnical functions due to one-dimensional-hindered rotation.[46−50] A correction of 0.6 kcal/mol to the ΔG_{1800} value for reaction 5 was calculated using the tabulated free energy differences for hindered rotation and harmonic oscillator given in ref 46 (Table 10). We have also considered the case of free internal rotation.[51] The calculated correction to the ΔG (1800 K) value is 4.6 kcal/mol using the free rotor approximation.

$$C_2H_4Cl_2 \rightarrow 2CH_2Cl \qquad (5)$$

TABLE 10: Calculated G2 and G2(MP2) Bond Dissociation Energy and Gibbs Free Energy for the C−C Bond Dissociation of 1,2-Dichloroethane (in kcal/mol)

$ClH_2C-CH_2Cl \rightarrow 2CH_2Cl$	G2(MP2)	G2
D_0 (0 K)	88.7	89.7
ΔG (1800 K)	5.7 (6.3)[a]	6.7 (7.3)[a]

[a] ΔG value calculated with the correction for hindered internal rotation[51] is given in parentheses.

The calculations of the dissociation of mustard, which take into account internal rotations about C−C and C−S bonds, require the determination of the all barrier heights for internal rotations and the moments of inertia. As recently shown by East and Radom,[52] calculations of the internal rotation barrier of species containing heteroatoms with lone pairs require the use of a large basis set like the 6-311+G(2df,p) or larger basis set and should be carried out at a correlated level. Sulfur mustard is a molecule with four internal rotations and couplings of the internal rotation modes should be addressed. For now there is no a practical approach for treatment of such a multirotor case. Furthermore, corrections for internal rotations in the products of dissociation should be made as well. And the problems described above for sulfur mustard, also take place for such products of its decomposition as $H_2CCH_2SCH_2CH_2$-Cl, $CH_2SCH_2CH_2Cl$, SCH_2CH_2Cl, and CH_2CH_2Cl. While accurate calculations of the free energy of the thermal decomposition of sulfur mustard will require further research, we can approximate corrections for the internal rotations in sulfur mustard and products of its dissociation. The data considered above for 1,2-dichloroethane allow us to suggest that a correction of 5 kcal/mol per internal rotation would roughly approximate the upper limit of such corrections to the ΔG (1800 K) values of the initial decompositions of sulfur mustard. Assuming that corrections for the internal rotations in the sulfur mustard molecule and those in the products of its unimolecular decompositions resulting in the cleavage of just one bond can almost compensate each other, an estimate can be applied for each breaking bond. This leads to an uncertainty in the ΔG (1800 K) values of about ±5 kcal/mol.[53]

(b) High-Temperature Decomposition of Mustard. The calculated bond cleavage enthalpies and Gibbs free energies show that sulfur mustard is surprisingly stable with respect to thermal decomposition even at 1800 K (Table 5, with an uncertainty of ±5 kcal/mol). At 1800 K the Gibbs free energy for homolytic C−Cl bond cleavage in **1b** yielding radical **5** and Cl is reduced to 19.4 kcal/mol while the BDE for heterolytic C−Cl bond rupture remains high at 101.5 kcal/mol. These data suggest that formation of the cyclic ethylene sulfonium ion intermediate **2** by loss of chloride anion will be restricted to the condensed phase. As in the high-temperature oxidation of long-chain alkanes,[3d] the preferred mode of homolytic dissociation of **1** is C−C bond breaking and at 1800 K the free energy for this bond cleavage to produce carbon radical **6** is 4.3 kcal/mol. Dissociation of the C−S bond will require temperatures in excess of 1800 K ($\Delta G = 6.8$ kcal/mol). We have also examined the BDE for both α- and β-CH homolytic bond cleavage forming radicals **3** and **4**. The free energy for α-CH bond cleavage is reduced from 94.0 to 29.8 kcal/mol at 1800 K. The corresponding energy requirements for homolytic cleavage of the β-CH bonds are slightly higher at 100.7 and 37.2 kcal/mol. These values demonstrate that the thermal decomposition of mustard would not be a spontaneous process (which requires $\Delta G < 0$) unless temperatures are approaching 1800 K.

TABLE 11: Calculated G2(MP2) Enthalpies and Gibbs Free Energies for the Subsequent Decompositions of the Primary Products of C−C, C−S, C−Cl, and C−H Bond Cleavages in Sulfur Mustard (in kcal/mol)

reactions	Δ*H* (298 K)	Δ*G* (298 K)	Δ*H* (1800 K)	Δ*G* (1800 K)
1a $Cl(CH_2)_2SCH_2CH_2$ (**5**) → SCH_2CH_2Cl (**7**) + CH_2CH_2	9.0	−0.3	2.7	−40.0
1b SCH_2CH_2Cl (**7**) + H → $HSCH_2CH_2Cl$ (**10**)	−89.4	−81.9	−90.4	−41.7
1c SCH_2CH_2Cl (**7**) → CH_2CH_2Cl (**8**) + S	70.7	60.2	71.0	7.3
2a $H_2CSCH_2CH_2Cl$ (**6**) → CH_2CH_2Cl (**8**) + $H_2C{=}S$	46.7	36.0	41.8	−13.6
2b CH_2CH_2Cl (**8**) → CH_2CH_2 + Cl	19.2	12.1	17.9	−22.5
3a $S(CH_2CH_2Cl)_2$ (**1b**) → $H_2C{=}CHS(CH_2)_2Cl$ (**11**) + HCl	16.9	5.4	14.8	−49.8
3b $H_2C{=}CHS(CH_2)_2Cl$ (**11**) → $H_2C{=}CHSCH{=}CH_2$ (**12**) + HCl	14.4	4.4	12.4	−46.1
3c $H_2C{=}CHS(CH_2)_2Cl$ (**11**) → $H_2C{=}CH$ + SCH_2CH_2Cl (**7**)	89.1	77.3	85.0	20.6

[a] Δ*H* and Δ*G* values were calculated without corrections for internal rotations, see text.

TABLE 12: Calculated G2(MP2) Gibbs Free Energies for the Decomposition of Sulfur Mustard Into Selected Small Fragments (in kcal/mol)[a]

reactions	Δ*G* (298 K)	Δ*G* (1800 K)
$S(CH_2CH_2Cl)_2$ → CS + $3CH_2$ + 2HCl	285.5	14.9
$S(CH_2CH_2Cl)_2$ → $H_2C{=}S$ + CH_2 + 2CH + 2HCl	362.2	97.2
$S(CH_2CH_2Cl)_2$ → H_2S + $2CH_2Cl$ + 2CH	324.9	77.1
$S(CH_2CH_2Cl)_2$ → H_2S + 4CH + 2HCl	490.8	157.2

[a] Δ*G* values were calculated without corrections for internal rotations, see text.

Therefore, in the absence of catalysis, robust environmentally sound decomposition of HD neccesitates an operating environment in excess of approximately 2000 K to insure that HD does not exit the designated destruction device. We will consider the role of metal catalyzed dissociation[43] in our next study.

Secondary Thermal Pathways of Sulfur Mustard Decomposition. We have also calculated the enthalpies and Gibbs free energies for various pathways for the secondary decomposition of sulfur mustard fragments. For example, the loss of a chlorine atom from sulfur mustard affords radical **5** ($ClCH_2CH_2SCH_2CH_2$) which can spontaneously lose ethylene with a ΔG_{1800} value of 40.0 kcal/mol (Table 11). The resulting radical **7** can abstract a hydrogen atom to form the partial decomposition product half-mustard, $ClCH_2CH_2SH$ ($\Delta G_{1800} = -41.7$ kcal/mol), which retains much of the toxicity of its parent. The loss of sulfur from **7** to form **8** ($ClCH_2CH_2$) remains highly endothermic even at 1800 K ($\Delta H_{1800} = 71.0$ kcal/mol). The loss of ethylene from **8**, however, is a facile process ($\Delta G_{1800} = -22.5$ kcal/mol) that leads to chlorine atom. Each of these intermediate radicals can abstract hydrogen from other fragments when concentrations are high and form a variety of PICs that may survive a combustion process. The dominant homolytic decomposition pathway remains C−C bond cleavage in **1b**. It leads to $ClCH_2CH_2SCH_2$ (**6**) which can readily eliminate $H_2C{=}S$ with a negative free energy (Table 11).

The initial carbon radicals formed in the high-temperature oxidation of alkanes decay into alkenes and hydrogen atoms.[3d] Similar formation of unsaturated compounds can be expected for the destruction of mustard. Indeed, another highly probable thermal process involves the concerted elimination of HCl from **1b** ($\Delta G_{1800} = -49.8$ kcal/mol, Table 11). However, this half-mustard derivative **11** still retains the β-sulfur ethyl chloride ($ClCH_2CH_2S-$) functionality that is responsible for the toxicity of this class of alkylating agent.[4a] Elimination of the second mole of HCl to yield divinylsulfide **12** is also a highly exothermic process ($\Delta G_{1800} = -46.1$ kcal/mol). Thermal decomposition of **1b** into selected minor fragments all have positive free energies at 1800 K (Table 12). In a similar fashion, the elimination of one and two moles of hydrogen from **1** affording **11** and **12** provides additional pathways for the thermal decomposition of sulfur mustard.

4. Conclusions

(1) In summary, even though HD is a highly reactive compound in the condensed phase, at high temperature the gas-phase unimolecular thermal decomposition of mustard is not a spontaneous process. Noncatalytic thermal destruction of sulfur mustard apparently is not feasible at temperatures up to 1800 K at least. The preferable high-temperature decomposition pathways involve C−C and C−S bond cleavages. (2) Environmentally robust decomposition/destruction demands operating conditions in excess of 2000 K to insure intrinsic safety in the absence of a catalyst. (3) A relatively high level of theory is required to accurately predict the bond dissociation energy resulting in radical fragments bearing adjacent lone pairs of electrons.

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Supporting Information Available: Harmonic frequencies of the *gauche* structure of ethanethiol calculated at the B3LYP/6-311G(d,p) and HF/6-31G(d) levels and the experimental values; G2 and G2(MP2) total energies of the species given in Tables 2, 3, and 11; G2(MP2) total energies of sulfur mustard and products of the C−Cl, C−S, C−C, and C−H bond cleavages in sulfur mustard; G2(MP2) total energies of the *trans* and *gauche* rotamers and the transition structures of 1,2-dichloroethane (5 pages). Ordering information is given on any current masthead page.

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